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Fogwater Chemistry in an Urban Atmosphere

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Analyses of fogwater collected by inertial impaction in the Los Angeles basin and the San Joaquin Valley indicated unusually high concentrations of major and minor ions. The dominant ions measured were NO_3^-, SO_4^{2-}, NH_4^+, and H^+. Nitrate exceeded sulfate on an equivalent basis by a factor of 2.5 in the central and coastal regions of the Los Angeles basin but was approximately equal in the eastern Los Angeles basin and the San Joaquin Valley. Maximum observed values for NH_4^+, NO_3^-, and SO_4^{2-} were 10.0, 12.0, and 5.0, meq l^{-1}, while the lowest *p*H observed was 2.2. Iron and lead concentrations of over 0.1 m*M* and 0.01 m*M*, respectively, were observed. High concentrations of chemical components in fog appeared to correlate well with the occurrence of smog events. Concentrations in fogwater were also affected by the physical processes of condensation and evaporation. Light, dissipating fogs routinely showed the highest concentrations.

INTRODUCTION

Laboratory [*Schwartz*, 1983; *Martin*, 1983; *Hoffmann and Jacob*, 1983] and field [*Cass and Shair*, 1980; *Cox*, 1974; *McMurry et al.*, 1981; *Smith and Jeffery, 1975*; *Wilson and McMurry*, 1981] studies have indicated that droplet-phase chemistry is important in SO_2 oxidation. Droplet-phase oxidation of SO_2 occurs, in part, via the following reactions

$$SO_2(g) \overset{K_H}{\rightleftharpoons} SO_2(aq) \quad (1)$$

$$SO_2(aq) \overset{K_{a1}}{\rightleftharpoons} H^+ + HSO_3^- \quad (2)$$

$$2HSO_3^- + O_2 \xrightarrow[Mn(II)]{Fe(III)} 2HSO_4^- \quad (3)$$

$$HSO_4^- \overset{K_{a2}}{\rightleftharpoons} H^+ + SO_4^{2-} \quad (4)$$

In Los Angeles, *Cass* [1975] observed a correlation between the occurrence of high sulfate aerosol levels during the afternoon and the presence of coastal fog and low clouds in the morning. The mean SO_2 to SO_4^{2-} conversion rate during July in Los Angeles is 6% hr^{-1} [*Cass*, 1981], whereas gas-phase reactions can account for, at most, conversion rates of 4.5% hr^{-1} [*Sander and Seinfeld*, 1976]. *Morgan and Liljestrand* [1980] reported that light misting rainfalls emanating from low stratus clouds in Los Angeles resulted in *p*H values as low as 2.9 with correspondingly high SO_4^{2-} and NO_3^- concentrations. *Waldman et al.* [1982] have previously reported *p*H values near 2.2 in urban fog. Furthermore, *Hegg and Hobbs* [1981] have reported S(IV) to S(VI) conversion rates of 4.0 to 300% hr^{-1} in wave clouds over western Washington.

In addition to its importance as a chemical reaction site, fog may exert a significant influence on scavenging and deposition, on human health, and on vegetation. Fog forms in the ground layer where gases and aerosols are most concentrated. Because fog droplets are approximately 100 times smaller than rain drops, they should be more concentrated than rain, and mass transfer should not limit the kinetics of fog droplet reactions [*Schwartz*, 1983; *Baboolal et al.*, 1981].

In light of these results and the expectation that fog droplets (or the fine aerosol remaining after fog has evaporated) are sites for rapid conversion of SO_2 to SO_4^{2-} we began a study to characterize the chemical composition of fogwater. Because of the physical similarity to clouds, fog is expected to exhibit the same chemical processes occurring in clouds and, to some degree, aquated submicron aerosols. Information about the chemistry of fogwater may be applicable to the broader questions about ambient acid formation and acidic precipitation. The role of fog in the nocturnal chemistry of SO_2 has been examined by *Jacob and Hoffmann* [1983].

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METHODS

Fogwater was collected with a rotating arm collector (RAC), which was modified from an original design reported by *Mack and Pilie* [1975]. A 67.5-cm-long, Teflon-coated steel tube with 10 × 0.95 cm slots milled into opposite sides at each end of the tube is rotated at 1700 rpm with a 1.5-HP induction motor. This rotation imparts a relative velocity of ~50 m/s to the slots. Droplets impact in the slots and are driven by centrifugal force into 30-ml polyethylene bottles attached at the ends of the arms. During operation, the pivot of the arm is 1.4 m above ground level. Based upon changes in particle-size distributions measured with a laser optical particle counter during operation in a cloud chamber, the RAC was determined to have a lower-size cut of ~8 μm [*Jacob et al.*, 1982]. The bulk of liquid water in fogs is contributed by droplets larger than 8 μm, but droplets smaller than 8 μm may be more concentrated than those that are actually collected. Consequently, the concentration of species in fogwater may be slightly underestimated. With this design, up to 2 ml min^{-1} of fogwater has been collected during dense fog and 0.1 to 1.0 ml min^{-1} during lighter fog. Collection efficiency under these conditions is estimated to be greater than 80%, based on laboratory calibration. We are currently working on a fog sampler with a lower-size cut in order to characterize the chemistry of the smaller fog droplets.

SITE DESCRIPTIONS

Figure 1 indicates the sites at which fogwater was collected. The Pasadena site, which is located on the roof of a four-story building on the Caltech campus, is in a predominantly residential neighborhood 25 km north of downtown Los Angeles. There are no major pollutant sources in the immediate vicinity. The Lennox site was selected because of its close proximity to both industrial and mobile pollutant sources and its high frequency of marine fog in late autumn: it is situated on the roof of a one-story building at a busy intersection within 100 m of a

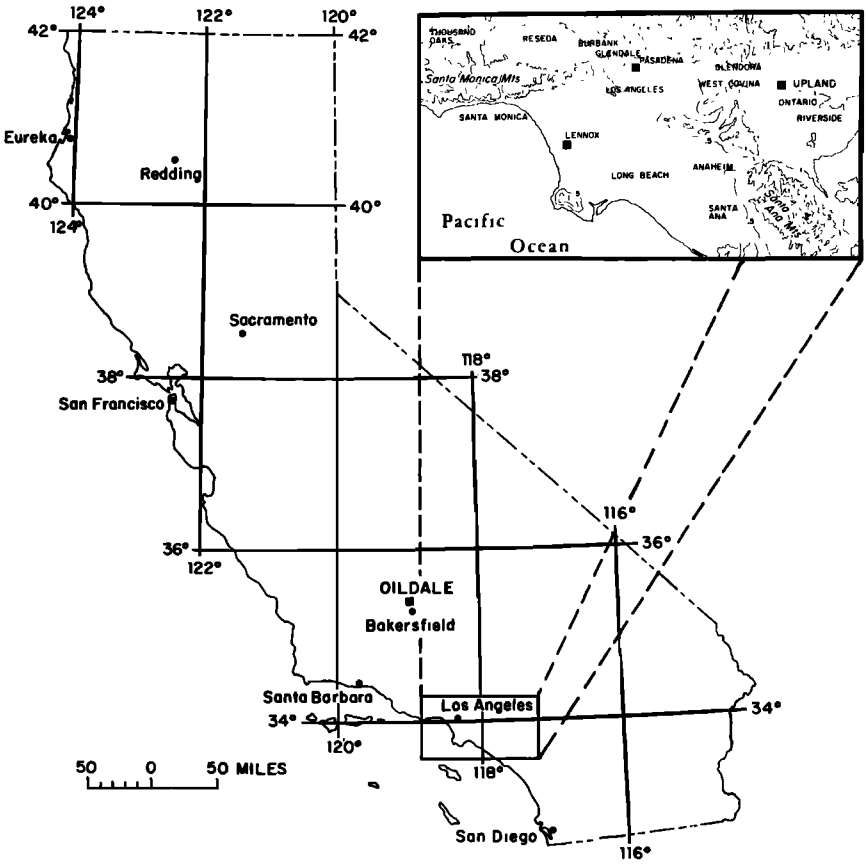

Fig. 1. Map of fog sampling sites in Southern California. Los Angeles area sites are indicated on the inset.

major freeway and 6 km from the ocean. Major point sources near the Lennox site include an oil refinery, power plant, Los Angeles International Airport, and several other industrial facilities.

The Oildale site, near Bakersfield, is in an area with higher sulfur emissions from secondary oil recovery operations and is subject to extensive fog ('Tule fog'), which persists throughout the San Joaquin Valley during the early winter. The sampler was placed on the roof of an air-quality monitoring station (about 4 m aboveground). Upland is 60 km NE of downtown Los Angeles. A steel plant and several other heavy industries are located within 30 km of this site, which is also on the roof of an air-quality monitoring station in a residential area.

Fog Patterns

In Los Angeles, fog generally occurs during two distinct periods: November through January and April through June. At the two inland sites, Pasadena and Upland, fog occurs sporadically in the night and early morning throughout the fog seasons. Fogs along the coast tend to form repeatedly for several nights, lifting for only part of the day. In the San Joaquin Valley, fog forms for extended periods during the early winter months and often persists throughout the day.

Analytical Methods

The sample-handling and analytical protocol is illustrated in Figure 2. Analysis of the sample began as soon as collection ended; measurement of *p*H and separation of preserved aliquots was completed within 30 min. In the field, samples were stored over ice, then refrigerated when brought back to the laboratory; *p*H was determined in the field with a Radiometer PHM 80 meter. Sulfite was preserved by addition of CH_2O at *p*H 4 to form hydroxymethanesulfonic acid (HMSA) [*Dasgupta et al.*, 1980; *Fortune and Dellinger*, 1982]; 3,5-diacetyl-1,4-dihydrolutidine (DDL) formed by reaction of formaldehyde and acetyl acetone in the presence of NH_4^+ [*Nash*, 1953] is stable for at least 7 days [*Rietz*, 1980]. Sulfite is known to interfere with this reaction [*Nash*, 1953], but no correction was made. Addition of HNO_3 to achieve a concentration of 0.16 *M* was used to stabilize an aliquot for trace-metal analyses. Beginning with the Oildale samples, aliquots were filtered through 0.4-μm Nuclepore membranes in the field. Because of extremely high cation and anion concentrations in fogwater, samples usually had to be diluted before analysis. With sample dilution, complete analyses of volumes as small as 5 ml was practicable.

Major cations were determined on a Varian AA5 atomic absorption spectrophotometer by using an air-acetylene flame. Lanthanum was added to the entire aliquot used for AAS in order to release calcium and magnesium. Ammonium was determined by the phenol-hypochlorite method [*Solórzano*, 1967]. Anions were determined by ion chromatography (IC), using a 3-m*M* $NaHCO_3$/2.4-m*M* Na_2CO_3 eluent. Aliquots of sample were spiked to give the same HCO_3^-/CO_3^{2-} concentration as the eluent in order to eliminate the water dip that interferes with F^- and Cl^- peaks. *Galloway et al.* [1982] suggest that low molecular weight carboxylic acids are present in rainwater. Considering the high aldehyde concentrations observed in fogwater, it is likely that the corresponding acids are present as well. If present, these acids would be a positive interference with fluoride. The absorbance of DDL formed

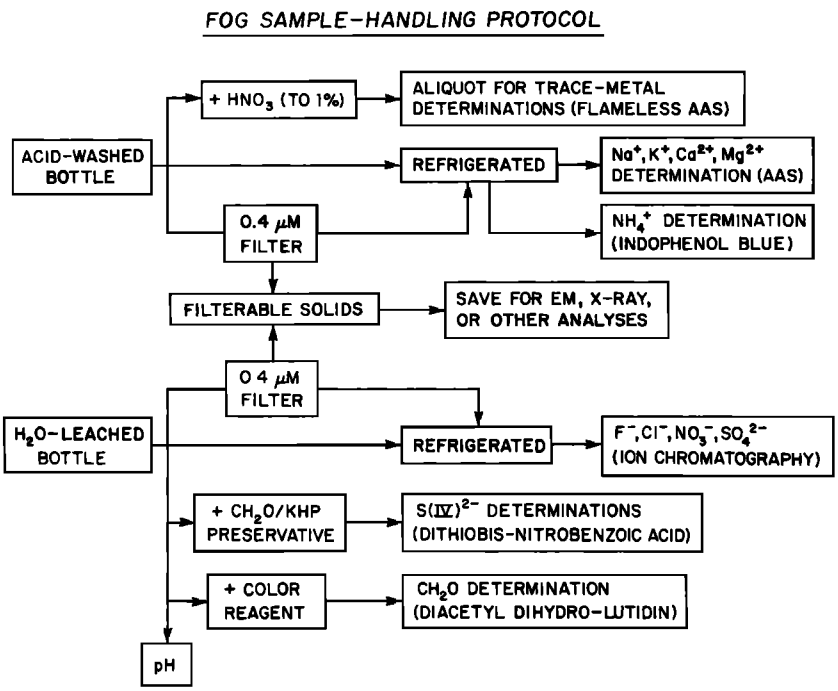

Fig. 2. A schematic flow diagram indicating fog sample-handling protocol and analytical procedures.

from CH_2O was measured at 412 nm on a Beckman Acta III spectrophotometer.

The preserved solution for S(IV) was injected into the IC and eluted with 1 m*M* KHP [*Dasgupta et al.*, 1980]. Because the F^- and Cl^- peaks coeluted with the hydroxymethanesulfonate (HMSA) using this eluent, the S(IV) in the samples could not be directly quantified. Instead, S(IV) was taken as the difference between the SO_4^{2-} concentration in the preserved aliquot and the SO_4^{2-} concentration in the unpreserved aliquot, measured by the usual IC methods. The first value would be SO_4^{2-} only, the second would be the sum of SO_4^{2-} and SO_3^{2-}. After December 7, S(IV) was measured by a colorimetric method, using 5,5', Dithiobis-(2-nitrobenzoic acid) DTNB [*Humphrey et al.*, 1970]. Trace metals were determined by flameless atomic absorption (Varian AA6 equipped with a CRA 90 or Perkin-Elmer 360 with a HGA 2100). Gas-phase concentrations of SO_2, NO_x, O_3 were made continuously at the Lennox, Upland, and Oildale sites by conventional instrumental methods.

RESULTS

Table 1 describes the conditions before and during the fog sampling. Samples from Pasadena were collected both after

TABLE 1. Description of Conditions During and Before Fog Sample Collection

Site	Date	Sampled Interval, hr	Conditions During Fog	Prior Conditions
Pasadena	November 15, 1981	2040–0115	Light wind SSW–N; sampled beginning to end of fog.	Fair, good air quality.
Pasadena	November 23, 1981	2320–0130	Light S–SE wind; 14°–12°C; fog thickened to near drizzle; sampled beginning to end of fog.	Hazy and smoggy.
Lennox	December 7, 1981	2305–0840	Light westerly wind; traffic volume and ambient pollutants began to increase at 0530; missed first hour of fog, sampled until fog lifted.	Previous night foggy, smoggy during day, NO_x alert called (NO_x = 0.8 ppm).
Lennox	December 18, 1981	2315–0043	Light westerly wind; sampled from beginning of fog; fog persisted until morning.	Previous night foggy; high NO_x levels during day.
Pasadena	December 20, 1981	745–845	Light northerly wind; 10°C; fog began before 0700; sampled until fog lifted	Previous day was fair.
Oildale	January 14, 1982	0200–0750	Light southerly wind; 3°–4°C, thin fog.	Overcast all of preceding day; dense fog on previous night.
Pasadena	January 17, 1982	2130–2200	Sample collected as fog dissipated.	Smog and haze during the afternoon.
Upland	May 14, 1982	0630–0910	Light and variable wind, 12°C, thin fog.	Low clouds and ground haze throughout night.

TABLE 2. Concentration Ranges for Major and Minor Ions, Sulfite, and Formaldehyde Observed During Fog Events.

Location	Number of Samples in event	Date	pH	$\mu eq\ l^{-1}$										mg/l
				H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	SO_3	CH_2O, mg/l
Pasadena	4	Nov. 15, 1981	5.25–4.74	5.6–55	12–496	4–39	370	19–360	7–153	120	56–280	130–930	62–380	—	—
Pasadena	4	Nov. 23, 1981	4.85–2.92	14–1200	320–500	33–53	1290–2380	140–530	89–360	180–410	480–730	1220–3250	481–944	150–180	3.1–3.5
Lennox	8	Dec. 7, 1981	5.78–2.55	2–2820	28–480	6–156	1120–4060	49–4350	17–1380	115–395	111–1110	820–4560	540–2090	30–250	4.6–12.8
Lennox	3	Dec. 18, 1981	2.81–2.52	1550–3020	80–166	19–40	950–1570	73–190	43–99	180–500	90–197	2070–3690	610–1970	—	—
Pasadena	1	Dec. 20, 1981	3.75	178	51	373	1773	217	78	242	161	1000	450	—	—
Oildale	3	Jan. 14, 1982	3.07–2.90	850–1260	151–1220	39–224	4310–9750	165–1326	20–151	126–242	203–592	3140–5140	2250–5000	440–710	6.1–14.4
Pasadena	1	Jan. 17, 1982	2.25	5625	2180	500	7960	2050	1190	637	676	12000	5060	—	—
Upland	3	May 14, 1982	2.88–2.22	1320–6310	1220–5200	96–482	2329–6312	596–4218	321–1816	168–342	654–1110	4240–10660	2760–4890	446–592	6.1–8.6

clean air days and smoggy days. The fogs in Lennox followed smoggy days. Oildale samples were collected during a period of extensive and persistent fog in the San Joaquin Valley. Samples at Upland were collected after dawn, when the haze that had been present during the night thickened enough to be collected.

The high and low concentrations of major ions, sulfite, and formaldehyde in fogwater during eight fog events are presented in Table 2. Concentrations of most ions in the second set of Pasadena samples, which followed a smoggy day, were higher than in the first Pasadena fog event. At Lennox the concentrations of major ions in fog were even higher than the Pasadena samples. Some of the fog samples from Lennox contained significant amounts of suspended solids. The greatest amount was in the final sample taken from the December 7 fog event during morning rush hour as the fog was dissipating.

The present sampling method does not differentiate between particles within droplets and particles greater than 8 μm that are independent of water droplets. Because the minimum size for activating condensation nuclei in ambient fog is much smaller than the collector cutoff size, most particles collected in fog, with the exception of hydrophobic material, can be assumed to be associated with droplets.

A single fogwater sample collected in Pasadena on January 17 had exceptionally high concentrations. The sulfate and nitrate concentrations were the maximum values observed in any fog. Fogwater collected in Oildale also had very high nitrate and sulfate concentrations as well as the highest NH_4^+, CH_2O, and S(IV) concentrations. The Upland fog samples were also characterized by high levels of acidity and acidic anions.

Concentrations of trace metals in the fog samples were also elevated, as shown in Table 3. During some of the fog events, metal concentrations varied over an order of magnitude. The usual pattern was for high concentrations at the beginning and end of the event. Lead and iron concentrations exceeded 1.0 mg L^{-1} (0.01 m*M*) on occasion.

The anion-to-cation ratios were close to unity for most of the samples, but there were discrepancies in some samples. In light of the large dilutions necessary to bring high concentrations down into suitable analytical ranges, the ion balances were reasonable. There were apparent excesses of cations in some of the samples that had large quantities of particles present. Calculation of the ion balance by using the concentrations of cations in filtered aliquots yielded better results. The aliquot for anions was routinely filtered prior to injection into the IC. This does not explain the apparent anion deficiency (or cation excess) in the fogwater samples collected from Oildale. The inclusion of SO_3^{2-} in the anion sum does not completely make up the deficit either, however, sulfite in aliquots from these samples was not measured immediately. Even though preservation techniques were used, sulfite may be underestimated. Considering the high concentrations of aldehydes, it is probable that the corresponding carboxylic acids were present in the fogwater; this would account for some of the apparent anion deficiency. Other factors that may contribute to poor ionic balances are losses of ions to particle surfaces via sorption and formation of adducts and complexes of indeterminant charge.

Discussion

Figure 3 presents the ionic composition of individual fog samples as a function of time. Concentrations of all ions decrease sharply during the first few hours of the fogs in Lennox; however, the ionic proportions do not change appreciably. In most cases, concentrations in the fogwater rose as the fog

TABLE 3. Ranges of Selected Trace-Metal Concentrations in Fog Samples

Site	Date	$\mu g\ l^{-1}$				
		Fe	Mn	Pb	Cu	Ni
Pasadena	Nov. 15, 1981	90–2,100	18–160	250–270	1–15	2–21
Pasadena	Nov. 15, 1981	920–1,770	34–56	1,310–2,540	88–140	8–14
Lennox	Dec. 7, 1981	356–23,700	19–810	820–2,400	9–150	2–52
Lennox	Dec. 18, 1981	1,020–2,080	25–81	1,700–2,350	84–1,400	32–54
Pasadena	Dec. 20, 1981	340	42	156	—	—
Oildale	Jan. 14, 1982	240–6,400	97–800	241–366	45–401	124–586
Upland	May 14, 1982	—	430–570	1,690–2,400	156–185	155–213

Number of samples per event is the same as for Table 2.

dissipated. The short duration fogs, which were usually very light fogs that resulted in low collection rates, also had high concentrations. Physical processes of droplet growth by accretion of water vapor, followed by evaporation, appear to account for this pattern.

Dilution by droplet growth could take place without any appreciable change in liquid water content (LWC) if the sedimentation rate was high enough to balance the condensation rate. Work by *Roach et al.* [1976] suggests that a significant portion of the liquid water formed during a fog event is lost, presumably to ground surfaces. During the periods over which concentrations were decreasing, collection rates, which are a function of LWC, remained constant. Advection of more dilute fog could account for this as well.

In Figures 4 and 5 the concentration of selected ions, normalized to their initial concentration, are depicted. If physical factors are responsible, the patterns will be nearly identical for ions that are controlled by the same factors or have common sources. The nearly hundredfold increase in Ca^{2+} and Mg^{2+}, and the concomitant drop in H^+ concentration in the final two samples collected in the December 7 fog at Lennox, coincided with morning rush hour traffic, which would generate a large amount of road dust. Concentrations of other ions were increased during that period, as a result of evaporation, but not to the extent that Ca^{2+} and Mg^{2+} increases (25 times their initial concentrations); $[Na^+]$ and $[Cl^-]$ increased by a factor of 5, and $[SO_4^{2-}]$, $[NO_3^-]$, and $[NH_4^+]$ returned to their initial concentrations. Acidity was nearly neutralized at the end of this fog event. In association with the increased $[Ca^{2+}]$ and $[Mg^{2+}]$, an increase in suspended particles, [Pb] and [Fe], was observed at the same time as a rise in CO levels at Lennox, coinciding with the morning traffic. Transfer of gaseous NH_3 into the droplets could account for the increase in $[NH_4^+]$ and simultaneous drop in $[H^+]$ during the December 7 Lennox fog event, while the other ions were maintained at constant concentrations. However, if the NH_3 had been present when the fog formed, it would have been immediately scavenged because of its high solubility at low *p*H. Unless there was a local source for NH_3, advective transport must be invoked to account for the apparent increase in $[NH_4^+]$.

In Pasadena, $[H^+]$ and $[NO_3^-]$ simultaneously increased while the other ions were decreasing. This may be evidence for the nocturnal formation of HNO_3 via the following reactions [*Graham and Johnston*, 1978]:

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (5)$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad (6)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \quad (7)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \quad (8)$$

Alternatively, the increase in HNO_3 could result from scavenging or diffusion of fine aerosol to the droplets or by advection of fog with higher NO_3^- concentrations.

In nearly all the cases the dominant ions in the fog samples were NO_3^-, SO_4^{2-}, H^+, and NH_4^+, which are the major components of secondary aerosol in Los Angeles [*Cass*, 1979]. These ions account for over 90% of the solutes in the initial stages of the Lennox samples. The highest concentrations were observed when the fog was preceded by smoggy days. Because secondary aerosols are effective condensation nuclei [*Barrett et al.*, 1979], they will exert a considerable influence on the composition and concentration in fogwater. When the concentration of secondary aerosol is high, the subsequent fogwater will also have high concentrations. The fraction of NO_3^- and SO_4^{2-} neutralized by NH_3 (measured in terms of NH_4^+) will largely determine the free acidity of the fog that first deliquesces. In this connection it is noteworthy that the initial fogwater samples collected at Lennox are the most acidic, and subsequent samples during the event are progressively more neutral, while at Pasadena and Upland the converse is true.

If HNO_3 and NH_3 were present when the fog initially formed, they would be scavenged rapidly as well and influence the fogwater composition [*Jacob and Hoffmann*, 1983]. However, the combination of cooler temperatures and higher humidity before the onset of fog will probably force NH_3 and HNO_3 to condense into the particulate phase [*Stelson and Seinfeld*, 1982; *Stelson*, 1982], which can be scavenged via nucleation or diffusion as the fog forms.

Figure 6 is a conceptualization of the condensation/evaporation cycle for fog droplets and illustrates the link between fogwater chemistry and the chemistry of smog and haze aerosol. High atmospheric concentrations of aerosol precursors appear to result in highly concentrated fogwater. Likewise, dissipation of highly concentrated fog results in very concentrated and reactive aerosol. The high trace-metal content in fogs would catalyze SO_2 oxidation. This link between fog and the subsequent aerosol can be seen in the correlation reported by *Cass* [1975] between morning fog and high humidity and high aerosol sulfate concentrations in the afternoon.

The Role of Aldehydes in Fog Droplets

Aldehydes are released as primary emissions from combustion sources and are generated photochemically from hydrocarbons [*National Research Council*, 1981]. The peroxide radical is an important byproduct of these reactions. Aldehydes are photochemically destroyed, with $OH\cdot$ and $HO_2\cdot$ as byproducts. Intermediates in aldehyde reaction pathways also play a role in the gas-phase reaction networks of SO_2 and NO_x.

Concentrations of formaldehyde as high as 0.5 m*M* were present in the Los Angeles fogwater samples. Other aldehydes,

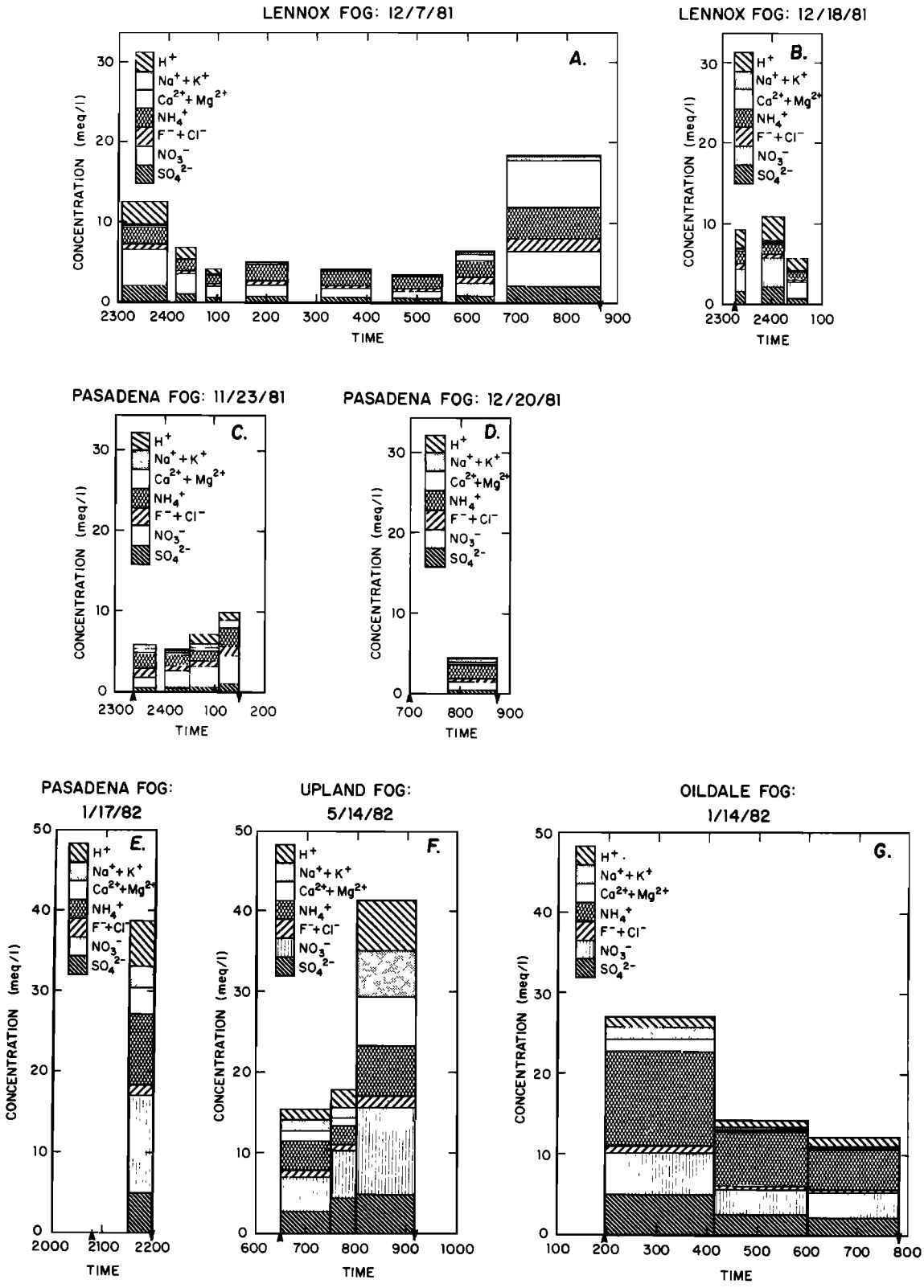

Fig. 3. Ionic composition as a function of time in sequential fog samples. Sampling interval is indicated by the width of each bar. The times of fog formation and dissipation are indicated by arrows.

such as acetaldehyde and benzaldehyde, are present in the Los Angeles atmosphere [*National Research Council*, 1981; *Grosjean*, 1982], and their presence in fogwater samples at comparable concentrations has been confirmed by the hydrazone derivative method [*Fung and Grosjean*, 1981]. Aldehydes react with HSO_3^- according to the following general stoichiometry:

$$HSO_3^- + RCHO \rightleftharpoons RHOCHSO_3^- \quad (9)$$

The formation constant for the formaldehyde-bisulfite addition complex, HMSA, has a maximum of about 10^5 between

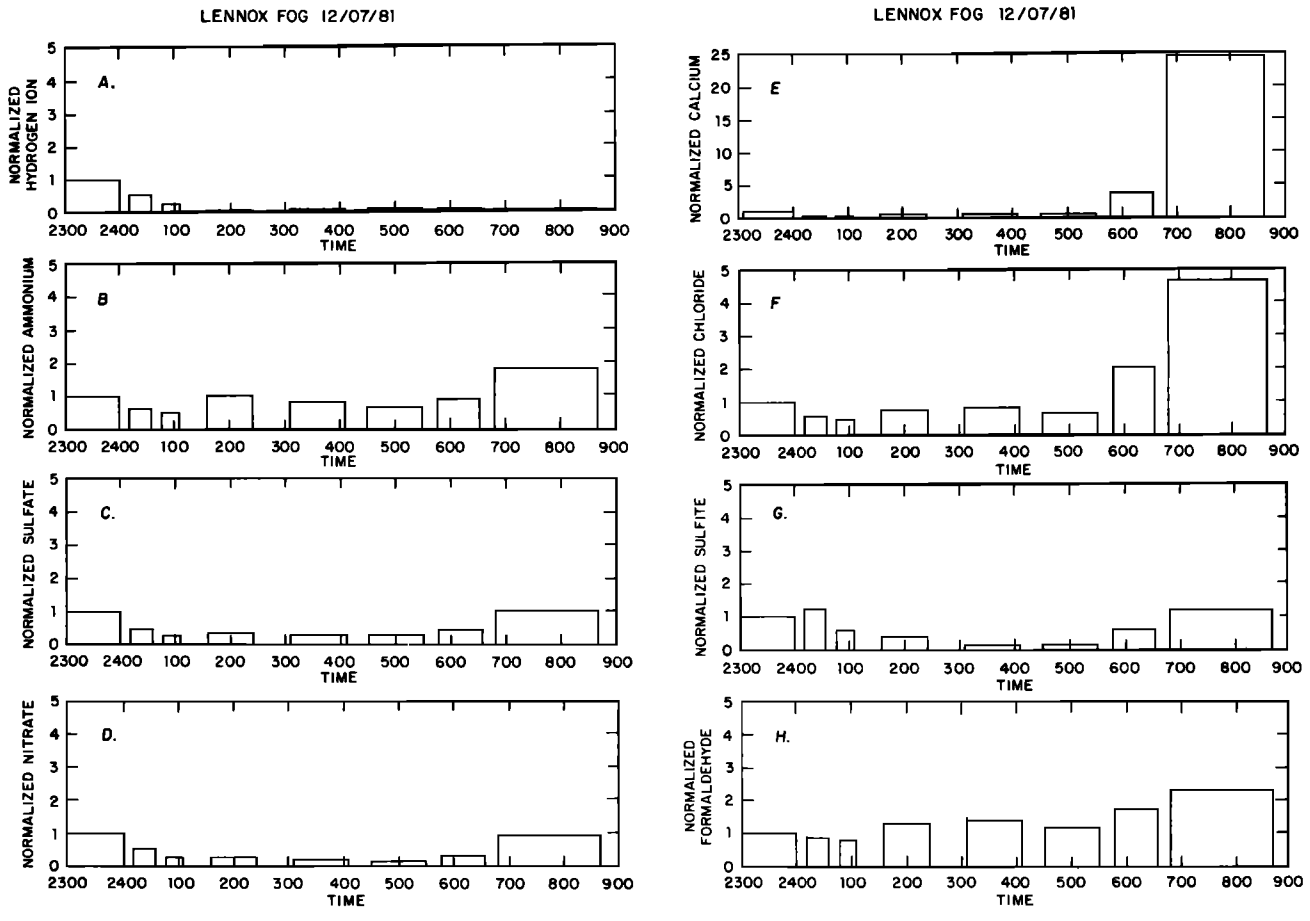

Fig. 4. (*a–h*) Nondimensional concentrations of individual ions in fog collected on December 7–8, 1981, at the Lennox sampling site. Concentrations are normalized for each component with respect to the concentrations in the initial sample (i.e., $\hat{C}_i = C_i/C_{i,0}$). Note the differences in scale. Sampling interval indicated by the width of each bar. NA indicates that a sample was not analyzed. Magnesium and sodium, which are not shown, were nearly identical to Ca^{2+} and Cl^-, respectively.

*p*H 4 and 6 and drops to 10^3 at *p*H 9 [*Dasgupta et al.*, 1980]. *Stewart and Donnally* [1932] observed a similar pattern for the formation of the benzaldehyde-S(IV) adduct. They also observed an interaction between temperature and *p*H. At low *p*H the temperature dependence of the equilibrium was stronger than at high *p*H. Low temperature increased the stability of the complex. The molar ratio of formaldehyde to S(IV) in the fog samples ranged from 0.9 to 17. Using Dasgupta's constants, the free S(IV) concentration in the fog ranges from 5% to 60% of the total. The equilibrium partial pressures of SO_2 and CH_2O, required to achieve the S(IV) and CH_2O values measured in the fogwater, were calculated from the following mass balance relationships:

$$[\text{S(IV)}] = [SO_2(aq)] + [HSO_3^-] + [SO_3^{2-}] + \sum_{i=1}^{n}[R_i\text{CHOHSO}_3^-] + \sum_{j=1}^{m}[M_jSO_3] \quad (10)$$

$$[R_i\text{CHO}]_T = [R_i\text{CHO}] + [R_i\text{CHOHSO}_3^-] \quad (11)$$

where R_iCHO represents aldehydes forming sulfonic acid adducts, and M_j represents first-row transition metals forming stoichiometric sulfite complexes, Using the appropriate conditional equilibrium expressions for the concentration of the sulfonic acid adducts of CH_2O, CH_3CHO, C_7H_6O, and the sulfitoiron(III) complex, and ignoring other S(IV) adducts and complexes because of their low potential concentrations, gives

$$[\text{S(IV)}] = K_HP_{SO_2}\left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}K_{a2}\beta}{[H^+]^2}\text{Fe(III)}] + \sum_{i=1}^{n}\frac{K_{a1}}{[H^+]}[R_i\text{CHO}]K_{Ai}\right) \quad (12)$$

$$[R_i\text{CHO}]_T = K_H{}'P_{R_i\text{CHO}}\left(1 + \frac{K_{a1}K_HP_{SO_2}}{[H^+]}K_{Ai}\right) \quad (13)$$

$$[\text{Fe(III)}]_T = [\text{Fe(III)}] + [\text{Fe(III)SO}_3^-] \quad (14)$$

where β is the formation constant for an Fe(III) – S(IV) complex; $K_H{}^i$ is Henry's Law constant for R_iCHO; K_H is Henry's Law constant for SO_2; K_{a1} and K_{a2} are acid dissociation constants; K_{Ai} is the bisulfite adduct formation constant, $P_{R_i\text{CHO}}$ and P_{SO_2} are partial pressures.

Substitution of the aldehyde and metal mass balances into (12) gives

$$[\text{S(IV)}] = \frac{K_HP_{SO_2}}{[H^+]^2}\left[[H^+]^2 + K_{a1}[H^+] + \frac{K_{a1}K_{a2}\beta[\text{Fe(III)}]_T[H^+]^2}{([H^+]^2 + \beta K_{a1}K_{a2}K_HP_{SO_2})} + \sum_{i=1}^{n}\frac{K_{a1}K_{Ai}[H^+]^2[R_i\text{CHO}]_T}{(H^+ + K_{a1}K_{Ai}K_HP_{SO_2})}\right] \quad (15)$$

The appropriate equilibrium constants are given in Table 4.

In the absence of adduct formation the equilibrium partial pressures of CH_2O calculated from fogwater data range from 16 ppb to 76 ppb, which are reasonable values for the Los Angeles atmosphere [*Grosjean*, 1982]. Adduct formation would lower the equilibrium partial pressure. The highest values of S(IV) found in some fog samples cannot be completely accounted for by aldehyde and iron-complex equilibria alone. Measured sulfite is 4–5 times higher than the predicted equilibrium value, even with P_{SO_2} as high as 30 ppb at the Los Angeles sites or 50 ppb at Oildale, which are the highest values for those sites. The lower concentrations of S(IV), however, are comparable to the values predicted from equilibrium considerations. Stable organic and inorganic sulfite species in ambient aerosols have been demonstrated to exist [*Izatt et al.*, 1978; *Eatough et al.*, 1978]. Aldehydes may play an important role in the atmospheric chemistry of S(IV) as stabilizers that retard oxidation of S(IV), and possibly as sources of peroxides and free radicals through their photochemistry. More data on the aldehyde content of the atmosphere are necessary to ascertain their role in the heterogeneous chemistry of SO_2.

Nitrate to Sulfate Equivalent Ratios

As is indicated in Figure 7, $[NO_3^-]$ in Pasadena and Lennox was about 2.5 times $[SO_4^{2-}]$; at Oildale and Upland the ratio was closer to 1 : 1. The nitrate to sulfate ratios in fogwater differ markedly from that observed in Los Angeles area rainwater [*Liljestrand and Morgan*, 1981]. In rainwater the equivalent ratio was less than 1 for coastal and central Los Angeles sites and increased to unity at Riverside at the eastern edge of the basin. Fogwater exhibited the opposite trend: $[NO_3^-]$ exceeded $[SO_4^{2-}]$ at the coastal and central Los Angeles sites and decreased to near one at the most inland site (Upland). Beside the differences in their source strengths (NO_x emissions exceed SO_2 emissions by a factor of 2.5 in Los Angeles), there are important differences in the kinetics of their respective oxidations and scavenging processes, as is discussed by *Jacob and Hoffmann* [1983].

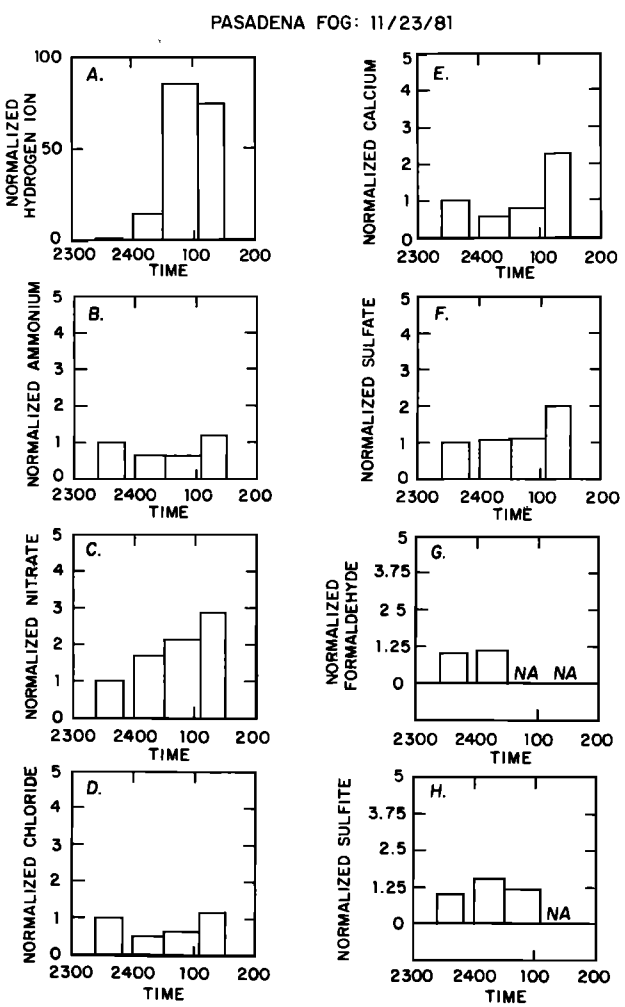

Fig. 5. (*a–h*) Nondimensional concentrations of individual ions in fog collected on November 23–24, 1981, at the Pasadena sampling site. The normalization procedure and scales are described in Figure 4.

Sodium Chloride Ratios

As Figure 8 illustrates, most of the fogwater samples had Na:Cl ratios near that of seawater. There were a few samples with excess Cl^-, which may be due to local sources. The highest excess of Cl^- was found in Lennox fog during morning rush hour, which suggests lead bromochloride salts from automobile emissions as a possible Cl^- source. Those samples also had high [Pb]. Two of the samples with excess Na^+ were collected at the beginning of fog events and may be affected by soil and dust. However, the other samples with excess Na^+ were extremely acidic. Reaction between marine aerosol and acidic gases or aerosol may be volatilizing HCl in the fog or the preceding aerosol as suggested by *Eriksson* [1960] and *Hitchcock* [1980]. The resulting fog would be deficient in Cl^-.

Comparison to Other Data

Fog and cloudwater ionic concentrations as high as in some of these samples have been observed previously (see Table 5). At many of the sites, *p*H values were in the range 3 to 4, but none were as low as the most extreme values for the Los Angeles area fogs. The concentration ranges for the cations Na^+, K^+, Ca^{2+}, and Mg^{2+} in other regions overlap with the concentration ranges observed in Southern California. The extreme values reported here, which were found in light fogs and in the Lennox sample that was laden with particles, are somewhat higher. Ammonium concentrations are comparable, but the extreme values observed in this study are about 10 times the maxima for previously reported data. Sulfate concentrations are comparable to other reported values, while nitrate concentrations are considerably higher in the California fogs, which is to be expected because of the dominance of NO_x emissions. Furthermore, high concentrations of HNO_3, which can be easily scavenged by fogwater, have been measured in the Los Angeles atmosphere [*Appel*, 1981].

Dense smog as a precursor gave rise to the most highly concentrated fogwater in Los Angeles. Other areas of the world subject to intense air pollution may also prove to have highly concentrated fogwater. Although ionic composition in the 1952 London fog was not measured, approximate calculations based on SO_2 emission rates, measured SO_2 concentrations, droplet residence time, and liquid water content [*Wilkins*, 1954*a*, *b*] gives SO_4^{2-} concentrations of 11 to 46 meq l^{-1}. For comparison, the extreme value measured during the winter of 1981–1982 in Southern California was 5 meq l^{-1}.

Implications

Highly concentrated fogwater can have several important environmental effects. Sedimentation and impaction rates of

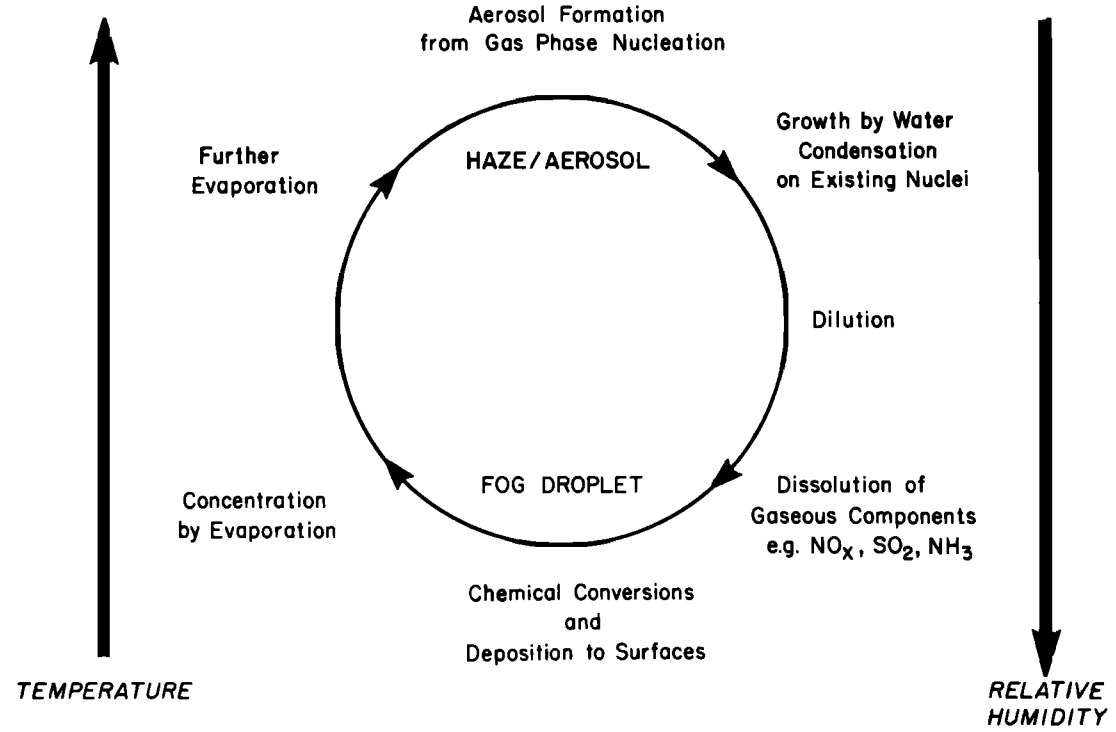

Fig. 6. A schematic diagram depicting the temperature and humidity dependence for fog formation and the apparent link between atmospheric gas phase and water phase chemistry.

TABLE 4. Equilibrium Constants Applicable to S(IV) and Aldehyde Chemistry

	K, M or M atm^{-1}	$\Delta H°$ 298, kcal mol	Reference
$SO_{2(g)} \overset{K_H}{\rightleftharpoons} SO_{2(aq)}$	1.245	−6.247	*Sillén and Martell* [1971]
$SO_{2(aq)} \overset{K_{a1}}{\rightleftharpoons} H^+ + HSO_3^-$	1.290×10^{-2}	−4.161	*Sillén and Martell* [1971]
$HSO_3^- \overset{K_{a2}}{\rightleftharpoons} H^+ + SO_3^{2-}$	6.014×10^{-8}	−2.23	*Sillén and Martell* [1971]
$CH_2O_{(g)} \overset{K'_H}{\rightleftharpoons} CH_2O_{(aq)}$	6.3×10^3	—	*Ledbury and Blair* [1925]
$CH_2O_{(aq)} + HSO_3^- \overset{K_{A,1}}{\rightleftharpoons} CH_2OHSO_3^-$	$\simeq 10^5$	—	*Dasgupta et al.* [1980]
$Fe^{3+} + SO_3^{2-} \overset{\beta}{\rightleftharpoons} FeSO_3^+$	$\simeq 10^{10} - 10^{18}$	—	*Carlyle* [1971]; *Hansen et al.* [1976]
$C_7H_6O + HSO_3^- \overset{K_{A2}}{\rightleftharpoons} C_7H_6OHSO_3^-$	$\simeq 10^5$	—	*Stewart and Donnally* [1932]
$C_2H_4O + HSO_3^- \overset{K_{A3}}{\rightleftharpoons} C_2H_4OHSO_3^-$	$\simeq 10^5$	—	by extrapolation

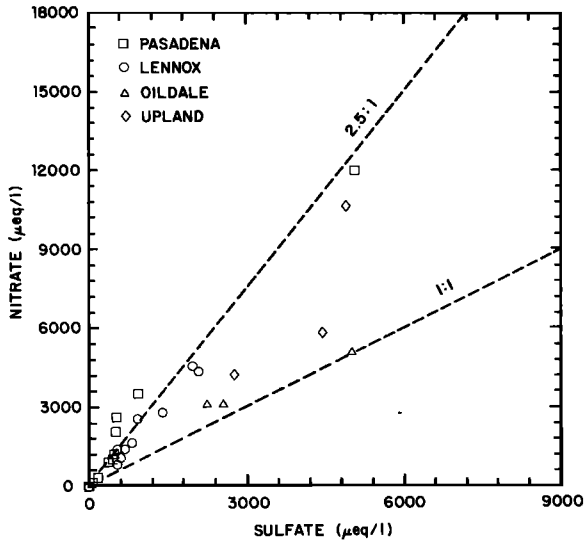

Fig. 7. Plot of nitrate and sulfate equivalent concentrations in fogwater. Dashed lines indicate 2.5 : 1 and 1 : 1 ratios.

fog droplets will be greater than for dry gas and aerosol. *Roach et al.* [1976] have calculated that up to 90% of the liquid water condensed during a fog event may sediment out on the ground. When winds accompany fog, interception of droplets by vegetation is also a major depositional pathway [*Schlesinger and Reiners*, 1974; *Lovett and Reiners*, 1982]. Measurement of rain and dry deposition fluxes alone may not adequately account for atmospheric loadings in regions where fog is frequent. Surface wetness from fog deposition may enhance deposition of SO_2 and subsequent oxidation to SO_4^{2-} (with a possible involvement of trace metals) [*Lindberg et al.*, 1979].

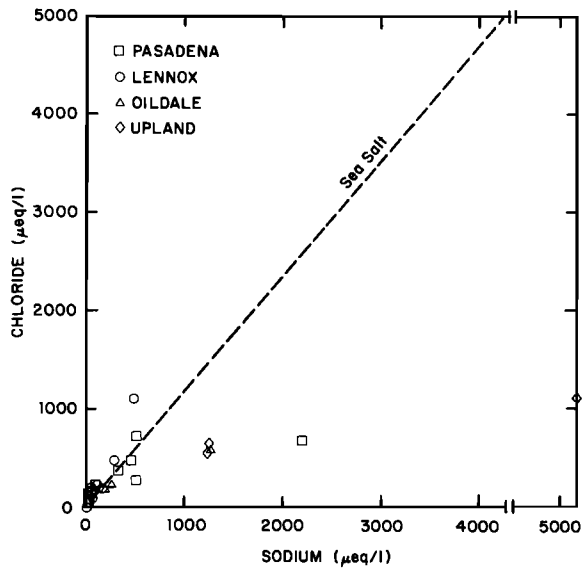

Fig. 8. Plot of sodium and chloride concentrations. Dashed line indicates the NaCl ratio in seawater.

Fogwater deposited on leaf surfaces is highly efficient in leaching ions from the leaves [*Tukey*, 1979] and may result in some plant injury. Experiments with acid mists show plant injury occurring at *p*H levels around 3 [*Jacobson*, 1980], which is typical of fogwater in parts of Southern California. Damage to building materials and metal surfaces is also possible from deposition of acidic fog. Corrosion of statuary and building materials has been observed in several locations throughout the world. The role of fog in this damage is not known, although research [*Metropolitan Museum of Art*, 1979] on the Horses of San Marco (ca. 100 B.C.) in Venice, Italy, indicates that fog and high SO_2 concentrations have resulted in significant damage during the last 50 years.

Historically, fogs have been implicated in a number of severe pollution episodes that caused increased human mortality [*Environmental Protection Agency*, 1971]. The most notable of these is the infamous London Fog of 1952 [*Wilkins*, 1954*a*, *b*], which caused 4000 excess deaths during the 5-day episode and 12,000 deaths over 4 months. Further research is needed to ascertain whether the fog caused mortality or was merely a consequence of the severe inversion conditions that caused a build up of toxic air pollutants, which were the true agents of mortality. Previous analysis [*Larsen*, 1970] suggested that these deaths correlated well with the product of gas-phase SO_2 and particle concentrations; however, sulfuric acid mists have been implicated [*Wilkins*, 1954*a*, *b*].

Conclusion

Fogwater in Southern California provides a propitious environment for the scavenging of particulate and gaseous forms of S(IV), S(VI), N(V), and N(−III); for the subsequent conversion of S(IV) to S(VI); and for the concomitant production of acidity. Unusually high concentrations of SO_4^{2-}, NO_3^-, NH_4^+, and H^+ were observed. The highest concentrations were observed during fog events preceded by smoggy days. Acidity caused by NO_3^- and SO_4^{2-} precursors was neutralized to some extent by scavenging of NH_3 and calcareous dust.

The physical processes of condensation and evaporation, along with scavenging and subsequent chemical conversion of reactive gas-phase components, appear to mutually control the temporal trends in fogwater composition. The apparent cyclical relationship between the occurrence of smog and fog in the Los Angeles basin is a manifestation of this phenomenon. The late night and early morning fogs, which form more readily in a particle-laden atmosphere, appear to accelerate and enhance smog production, visibility reduction, and particulate sulfate levels during the subsequent day. This relationship can be dubbed the smog-fog-smog cycle.

Clearly, more research is needed to elucidate the mechanisms by which fog-processed aerosols become highly reactive sites for daytime photochemical transformations. The role of aldehydes and transition metals in the transport and transformation of S(IV) in atmospheric water droplets needs to be explored more intensively. Furthermore, given the millimolar concentrations of some of the metal ions in urban fog, the effect of metal ion catalysts on important chemical transformations (e.g., S(IV) to S(VI)) needs to be considered more carefully in the development of quantitative air quality models for urban airsheds.

TABLE 5. Summary of Fog and Cloud Water Compositions

Location	Date	Type*	pH	μeq l^{-1}								Reference
				SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	
Mt. Washington, N.H.	1930–40	CF	3.0–5.9	4.2–1100		0–34						*Houghton* [1955]
Nantucket, Mass.	1930–40	MF	—	285–2600		650–5750						*Houghton* [1955]
Brooklin, Maine	1930–40	F	3.5–6.3	95–770		0–140						*Houghton* [1955]
SW of London	1960	C†	4.4–7.2	40	19	94	95	13	66	25	22	*Oddie* [1962]
Germany, Baltic Sea	1955–65	MF†	3.8	1860	900	1740	1500	240	750		2335	*Mrose* [1966]
Harz Mtn.	1955–65	CF†	5.1	775	450	205	295	85	220		710	*Mrose* [1966]
nr. Dresden	1955–65	UF†	4.2	3300	380	585			3180		2100	*Mrose* [1966]
Kiev, USSR	Dec. 1964	C	3.4–5.4	400–2060	17–200	115–325	80–215	30–130	40–535	16–160	235–1300	*Petrenchuk and Drozdova* [1966]
Mt. Noribura, Japan	July 1963	CF	3.4–4.3	230–1250	50–350	75–230	45–165	55–85			115–260	*Okita* [1968]
Mt. Tsukaba, Japan	Nov. 1963	CF	5.6–6.5	360–2065	11–75	295–1270	180–435	154			110–965	*Okita* [1968]
Puerto Rico	Nov.–Dec. 1967	C	4.9–5.4	75–190		150–1975				20–90	35–400	*Lazrus et al.* [1970]
Nova Scotia	Aug. 1975	MF		54–470		14–235	880–1240	43–50	38–69	42–77	9–72	*Mack and Katz* [1976]
Coastal California	Sep.–Oct. 1970	MF		77–490	24–235	96–1235	78–945	11–23	9–100	23–175	0–580	*Mack et al.* [1977]
Whiteface Mtn., N.Y.	Aug. 1976	CF†	3.6–3.9	52–140	140–215	1.7–3.1	2.3–11	13–20	10–20	2.2–6.1	32–89	R. A. Castillo et al. (unpublished manuscript, 1980)
	Aug. 1980	CF	3.2–4.0	32–806	7–192	1–14	1–7	1–6			4–197	*Falconer* [1981]
Los Angeles, Calif.	Jan. 80	C	4.6–6.8	5–400	0–445	1–760	2–50	1–70			0–230	*Hegg and Hobbs* [1981]

*Type of sample: F = fog; C = clouds aloft; CF = intercepted clouds; MF = marine fog; UF = urban fog
†Mean values of samples
‡Range of mean values; otherwise range of samples

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